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Environmental Health Center
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A STUDY OF TASTE AND ODOR PRODUCING CHEMICALS IN WASTES AND WATER SUPPLIES IN THE SOUTH LAKE MICHIGAN AREA

INTRODUCTION

Tastes and odors have been for many years a difficult problem in the drinking water supplies of the cities located on the south end of Lake Michigan. The cities located in this area that take their water from Lake Michigan include Chicago, Illinois, and Hammond and Whiting, Indiana. The taste and odor problems in this area are complicated by the fact that they may be associated with both natural biological growth and with industrial wastes. Previous reports by Baylis (1) and Bartuska (2) have described some of the measures that have been taken toward a solution of the problem.

During 1949 and 1950 a technique was developed in the laboratory of the Environmental Health Center at Cincinnati for concentrating the minute quantities of organic materials from water on small activated carbon filters with subsequent elution of the adsorbate for study (3). In view of the possibilities of the application of such a technique to the odor problem in the south area of Lake Michigan, a cooperative study was suggested to the interested authorities of the Indiana State Board of Health, the South District Filtration Plant of Chicago, a large oil refinery, the City of Whiting, Indiana, and the City of Hammond, Indiana.

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All agreed in conference to cooperate in such a study of the taste and odor producing compounds in the refinery waste effluents and the water supplies of the area. Accordingly, the carbon filter assemblies were shipped from the Center and were installed and operated locally by each cooperating organization. The details of collecting, eluting and studying samples of this type are to be found in a publication (3) by Braus, Middleton and Walton. (See reprint attached to this report).

SAMPLING POINTS

The sampling points at which the filters were installed and operated were as follows:

(1) Refinery Oil Separator Effluent.

(2) Indiana Harbor Ship Canal, Whiting, Indiana.

(3) Raw Water Intake, Whiting, Indiana Water Works.

(4) Raw Water Intake, Hammond, Indiana Water Works.

(5) Raw Water Intake, Chicago, Illinois South District Filtration Plant.

Data concerning the flow and dates of operation of the activated carbon filters are shown in Table 1.

ANALYSIS OF SAMPLES

Drying and Elution

The carbon was removed from the filters following the sample run and air dried at room temperature. The organic materials were desorbed from

the carbon with redistilled C.P. chloroform for a period of 50 hours in a modified Soxhlet apparatus. The chloroform extract was distilled to a low volume and the refractive index of the distilled chloroform was taken periodically. Values of the refractive index indicated that the distillate was substantially pure chloroform, suggesting the absence of volatile materials in appreciable quantities. The residual chloroform extract was then dried over anhydrous sodium sulphate, filtered and washed. The remainder of the chloroform was distilled off and the final extract was further dried in a vacuum over calcium chloride without resort to heat in order to minimize the loss of the more volatile constituents.

Quantities of Extract Recovered

The quantities in grams and parts per billion (p.p.b.) of extract recovered from the carbon filters are given in Table 2. Various factors may affect the quantities and kinds of material retained on the carbon. For example, the less soluble and less polar compounds are generally more strongly adsorbed. Thus polar groups such as OH, NH_2, etc., in an organic molecule tend to decrease adsorption from aqueous solution[4]. In an analogous manner larger molecules are more generally adsorbable than are smaller similar molecules. This may be due to the decreased polarity and decreased solubility of the larger molecules. Hence, as the carbon becomes saturated, materials of a more soluble and more polar nature would tend to be displaced in favor of less polar and less soluble compounds. Thus, oxygen, sulphur and nitrogen compounds generally tend to be displaced by hydrocarbons.

The hydrogen ion concentration of the water also affects the kinds of materials adsorbed. For example, organic acids that would not be adsorbed under alkaline conditions may be readily adsorbed at lower pH values. Conversely, a high pH favors the adsorption of basic organic amines. The organic acid or the organic base is more non-polar in the free state than in the combined state. When an organic acid and organic base are both present at a neutral pH, the adsorption of both are diminished.

The adsorption by carbon of the refinery waste occurred at a low pH. The carbon adsorption from the Indiana Ship Canal and from the three municipal raw lake water supplies was carried out from pH 7.0 to 8.0. There was no pH adjustment during the carbon adsorption procedure at any location in this study. The lower pH of the refinery waste water would have little effect per se on the adsorption of most of the neutral compounds. However, it would enhance the adsorption of organic acids and phenols but would reduce the adsorption of organic amines. In the case of the city water supplies, one could expect incomplete recoveries of acidic constituents. Tastes and odors of acidic materials other than phenols obtained from unrelated water supplies have been shown to be relatively innocuous (5). Little can be said at present concerning the nature of materials recovered from pre-alkalinized water supplies.

It should be noted that the filter from the refinery effluent was apparently saturated with organic material. This was evident from the strong odor emanating from the carbon as received. It has been our experience that a carbon not completely saturated with adsorbed organic

material is substantially free of odor. Even chlorinated phenolics adsorbed below the point of saturation of the carbon cannot be detected by odor. Because the carbon in this filter was apparently saturated, it is quite probable that some phenolics, amines, acids and sulphur compounds were displaced by more non-polar compounds. The extent to which this has occurred cannot at present be ascertained. Future work using filters at various stages of unsaturation of the carbon up to the point of complete saturation would throw light on this phase of the problem.

It is well at this point to consider just what materials the refinery effluent carbon may have adsorbed in relation to taste and odor producing substances. It is generally agreed that no single pattern of chemical structure serves to maintain even a trend of odor properties (6). Highly odorous material, however, tends to be more ether soluble and less water soluble. Conversely, most inodorous materials are more water soluble and less ether soluble. Referring again to the principles of polarity, non-polar compounds are more odorous and generally more strongly adsorbed on carbon. It may be concluded that a large portion of the odorous constituents present in the refinery effluent were retained by the carbon. Quantitative recovery of all odorous constituents, while definitely desirable, has not been attained. The fact that some odorous compounds may not have been recovered by the carbon should not greatly alter the general value of this procedure.

Properties of Extracts

The extracts from the oil separator effluent and the Ship Canal are black liquids. The odor, best described as "refinery type" or "gasoline-like", is extremely obnoxious and soon permeates the air of a large room when a bottle is opened to the atmosphere. The extracts from Whiting and Hammond raw waters are viscous, brownish colored liquids. The gross odor is much the same as the oil separator effluent extract and the Ship Canal extract. The Chicago water extract separated into two phases, the lower phase being much darker in color. The appearance of this extract was similar to the one obtained from Hammond. The odor is much less obnoxious and less intense than the other extracts. However, some of the same refinery characteristics are perceivable by smell. Details of taste and odor tests on these extracts will be found in another section of this report.

Quantitative determinations were made on the extracts for the elements carbon, hydrogen, nitrogen and sulphur. Oxygen values were obtained by difference. These ultimate analyses are a new approach in the field of industrial waste analysis and it is felt that greater insight is gained of the nature of the materials present in both industrial wastes and wastes obtained from contaminated waters. A sample of an extract from Cincinnati water was also tested for the same elements. This was done to secure comparative information on a water from a source other than Lake Michigan. It is to be noted that the Cincinnati water was breakpoint chlorinated which may have oxidized some of the organic sulphur present. Also, the calculation of oxygen by difference may not be valid due to the chlorination of the Cincinnati water from which the extract was obtained. Chlorinated organic

materials are probably present. The results of the elemental analysis are shown in Table 2.

The high percentage of carbon (84.9) and hydrogen (11.2) in the oil separator effluent extract is indicative of hydrocarbon material. The high percentage of hydrogen is indicative of aliphatic hydrocarbons and alkylated aromatics. Unsaturated hydrocarbons are also shown to be present by the permanganate and bromine tests.

In view of the fact that the carbon, hydrogen, sulphur and nitrogen analysis total 97.43 per cent in the refinery effluent extract and the group analysis shows the presence of some three per cent phenolics, which by definition contain oxygen, it is justifiable to assume the remainder as oxygen. In any case, the remainder may contain traces of halogen or phosphorous, but their presence or absence appears of little significance.

The hydrogen content of the organic extract from the Indiana Ship Canal is similar (10.7 per cent) to the value obtained on the refinery effluent. This extract shows a lower carbon content and a correspondingly increased oxygen content. This may indicate that some oxidation of the unsaturated portion of the original waste has occurred by contact with water or that other type wastes are present, or possibly both. Assuming the oxygen value obtained by difference to be correct, it can be seen that the analysis as shown for the Ship Canal fits rather closely that of a C_{10} to C_{12} acid. However, the laboratory study of this extract indicates that it is a complex mixture so it is unreasonable to assume that the extract is a rather pure substance such as a C_{10} to C_{12} acid. More likely there is a balance of aliphatic and aromatic hydrocarbons together with intermediate chain length acids as the products of oxidation. Support for this interpretation is offered by infrared studies.

The extracts from Whiting and Hammond appear to be very similar as judged from the elemental analysis. It will be noted that the hydrogen content (9.3 and 10.3 per cent) in these samples is very similar to the Ship Canal sample while the carbon content (74.4 and 76.4 per cent) is between the values obtained on the oil separator effluent and the Indiana Harbor Ship Canal. Again, it appears that the original waste has undergone partial oxidation to give rise to some carbonyl compounds or that other wastes are contributing carbonyl compounds. The high values of hydrogen in these extracts supports the belief that the oxygen is not integrally bound to the long chain hydrocarbons and exists independently of the main hydrocarbon fraction. Stated otherwise, these extracts appear to be aliphatic hydrocarbons contaminated by carbonyl compounds. The Chicago extract shows the lowest percentage of carbon (66.6) and a correspondingly increased amount of oxygen (22.23). This may be due to the greater time of contact of the wastes with the water resulting in increased oxidation of the original wastes. There is a possibility that other wastes may have influenced the results obtained at Chicago.

The organic sulphur analysis of the extracts may be of particular significance. A micro sulphur determination by one analyst resulted in 1.2 per cent in the refinery effluent as shown in Table 3. A macro determination of organic sulphur by another analyst using a Parr Bomb reported a value of 3.02 per cent. The reason for the discrepancy in these values is not known. Vacuum distillation of the neutral fraction of the refinery extract resulted in copious volumes of sulphur bearing gases which were released from the vacuum pump outlet.

The presence of organic sulphur compounds in the refinery waste was expected. Analytical confirmation of this fact and the proved presence of organic sulphur compounds in the adjacent water supplies indicated that the sulphur might serve as a tracer element in studies of this type. Certain reservations, however, at present are necessary in this interpretation and more research is needed on the sulphur content of carbon filter extracts from various waters.

A sulphur analysis was made on an extract from the Cincinnati water. As shown in Table 1, less than 0.2 per cent sulphur was found. Inspection of the other sulphur values indicates that the Lake Michigan samples contain from 6 to 10 times more sulphur than the Cincinnati water. It must be remembered, however, that the extract of the Cincinnati water was obtained from water which had been breakpoint chlorinated. Conceivably, oxidation of sulphur may have taken place and the sulphur content of this extract cannot be used as a standard of reference.

The organic sulphur in the refinery effluent may be present in greater amounts than that indicated by the present technique. Since the refinery filter was saturated it is reasonable to believe that the less polar compounds, e.g.,hydrocarbons may have displaced the more polar sulphur compounds. Consequently, it may be possible that more organic sulphur compounds are discharged into the lake from the refinery than is shown by this study. It should be noted that the carbon in the various city filters was unsaturated. Being unsaturated these filters would tend to retain more of the sulphur bearing materials. Perhaps this explains the relative relationships of these various sulphur analyses. It is obvious also that with the present stage of this technique, one cannot preclude the absence of other organic

sulphur bearing wastes especially if other sulphur containing wastes are discharged into this area. Very little is known about the sulphur contribution of the flora and fauna of Lake Michigan water. Additional research is needed to determine the kinds and quantities of organic sulphur compounds present in polluted and non-polluted waters.

Fractional Distillation

A sample of the oil refinery waste effluent extract was distilled under reduced pressure in a Penn-State semimicro fractionating column. A strong odor of sulphuretted gases was noted during the distillation. All of the fractions recovered had extremely obnoxious and nauseating odors. The mixture consisted of compounds of very similar boiling point range which were difficult to separate. Table 4 shows the boiling point range and some of the physical properties of the fractions distilled. Infrared studies on these materials indicate them to be principally hydrocarbons*.

Chemical Separation of Extracts

The extracts from the refinery separator effluent and the City of Whiting raw water were separated into acidic, basic, phenolic and neutral groups in accordance with the scheme outlined previously (3). The quantitative recoveries of these groups from the refinery sample and Whiting are shown in Table 5. It will be noted that the neutral group of compounds are present in the greatest quantities. A substantial amount (3.73 per cent) of phenol was recovered from the refinery samples.

(*) The infrared spectrograms of these individual fractions are not included in this report but are available upon request.

The unaccounted for portions of the oil refinery separator extract consists of materials lost in manipulations, amphoteric materials, ether insoluble materials and colloidal carbon. An unaccountable manipulative loss occurred with the Whiting sample and the separation could not be repeated due to insufficient sample material.

The ether insoluble and amphoteric materials are not considered important from the standpoint of taste and odor. This is because of the small fraction of the total extract represented by these constituents and because of their low taste and odor intensities. Moncrieff says "It is clear that odorous materials are generally more soluble in ether than in water and that sapid, inodorous materials are more soluble in water than in ether" (7). While not all amphoterics are ether insoluble the increase in the hydrocarbon portion of the molecule which may render an amphoteric compound ether soluble, at the same time generally detracts from the aromaticity of the molecule. Zwitterion formation in amphoterics generally diminishes odor as the molecule is now an inner salt. In addition, the polyfunctionality exhibited by amphoteric molecules generally decreases the taste and odor of a substance.

Infrared Spectra of Extracts and Components of Extracts

The extracts and certain of the group constituents of the extracts were examined for infrared absorption characteristics. These tests were made on a Baird Infrared Double Beam Recording Spectrophotometer. Attached to this report are the spectrograms of the raw extracts, the neutral fractions of the refinery separator extract, Whiting and Chicago, and three of the fractional distillates of the refinery separator extract. So far as is known, this is the first general application of infrared analysis to water pollution studies.

Interpretation of the infrared spectrograms is given below. These studies are intended to show the similarities and differences of the absorption spectra and the predominant chemical groups that are indicated in these materials. The interpretation will be confined to the portions of the spectrum above 1350 cm^{-1}. This is because of present limitations on frequencies below this value. Barnes et al [8] state: "At the present time, frequencies above 1350 cm^{-1} allow fairly definite assignments while those below 1350 cm^{-1} will necessarily be less definite because these vibrations generally involve all the atoms of a molecule rather than those of a specific part. Moreover, exceptions to any correlation will be found because the exact values of the frequencies are always dependent on the rest of the molecular substitutions or unsaturations, and accidental degeneracies will occur to split an expected single band into a doublet which will confuse the spectrum. However, the information which has already been gained has proved of great value in such applications as indicating the presence or, of equal importance, the absence of specific groups in an unknown material."

There is some latitude involved in these interpretations; however, chemical confirmation where it exists renders the interpretation more exact. The materials discussed are highly complex mixtures with little or no precedence of established procedure for interpretation. Consequently, conclusions are drawn from general infrared characteristics of pure compounds. It should be noted that absorption bands in Figures 1, 3, 5, 8 and 9 at 1215 cm^{-1} and 760 cm^{-1} are due to the presence of small quantities of chloroform.

Detailed examination of the spectrogram ~~of the spectrogram~~ of the refinery waste separator effluent extract (Figure 1) reveals the following information:

(1) Absorption in the range of 3300 cm^{-1} - 3600 cm^{-1} suggests the presence of free hydroxyl groups. Chemical isolation shows the presence of free phenols.

(2) The same region, i.e., 3200 to 3500 cm^{-1}, also indicates N - H bonds. The chemical isolation of very small amounts of amines and the low values of nitrogen found by analysis probably precludes this band being due to N-H groups. Consequently, this absorption band is due largely to OH.

(3) C - H frequencies occur between 2800 and 3200 cm^{-1}. This region is subdivided by the characteristic that the band is usually above 3000 cm^{-1} if the carbon atoms are unsaturated. In normal aliphatic compounds the bands usually occur below 3000 cm^{-1}. Strong absorption bands mostly below 3000 cm^{-1} are evident in this curve. This indicates high aliphatic content. Some aromaticity, though in much lesser amounts, appears evident.

(4) Absence of absorption bands between 2000 and 2300 cm^{-1} indicates the absence of C≡C, and C≡N groups.

(5) A very slight band in the region of 1850 to 1650 cm^{-1} indicates the virtual absence of anhydrides, esters, acids, ketones and aldehydes. The absence of carbonyl groups thus shows that the OH grouping found earlier is not due to the presence of acids.

(6) Aliphatic carbon-carbon double bond linkages occur between 1600 and 1660 cm^{-1}, if the bond is not conjugated. If it is conjugated with aromatic unsaturation the frequency drops to 1625 cm^{-1} whereas if full aliphatic conjugation occurs the frequency is near 1600 cm^{-1}. The relatively small absorption band on the refinery spectrogram may indicate unsaturation or C=C linkages to be present in moderately small amounts. The degree and kind of conjugation is not readily apparent from the spectrogram.

(7) The phenyl ring gives rise to absorption bands at 1600 cm^{-1} and near 1500 cm^{-1}. These bands are present in the refinery extract. Aromatic material is thus indicated.

Summary

The conclusion to be drawn from the above statement is that the refinery waste extract is composed chiefly of aliphatic and alkylated aromatic hydrocarbons.

Oil Separator Effluent Neutral Group (Figure 2)

(1) This spectrogram is very similar to that of the refinery separator extract spectrogram. One difference is the absence of the band noted in Figure 1 at 1215 cm^{-1} which is probably due to chloroform.

Summary

On the basis of the interpretation of Figure 1, this spectrogram (Figure 2) indicates a mixture of hydrocarbons with some unsaturated compounds being present.

Whiting, Indiana Raw Water Extract (Figure 3)

(1) Free OH is indicated by the absorption band in the 3300 cm-1 to 3600 cm-1 range though in small amounts.

(2) As stated previously, the C-H frequencies occur in the range between 2800 and 3200 cm-1. The strongest absorption is below 3000 cm-1. Consequently, greater aliphatic content would seem to be indicated.

(3) Carbonyl frequencies fall between 1650 cm-1 and 1850 cm-1. In this curve the carbonyl frequency occurs between 1670 cm-1 and 1750 cm-1. While some carbonyls tend to absorb in fairly definite and narrow wave lengths, it is difficult to place any real significance on the type or types present in this case. One might conclude that more than one type of carbonyl is present here because of the wide range of this band. The moderate intensity of this band indicates a moderate content of carbonyl. Some acids are also present because the neutral fraction shows a greatly diminished intensity of carbonyl bands.

(4) Aromatics are indicated by the bands at 1600 and 1500 cm-1 though in relatively smaller amounts.

(5) Unsaturation of aliphatic materials may be indicated but these bands are difficult to distinguish in the presence of aromaticity.

Summary

This material appears to be largely composed of hydrocarbons contaminated with carbonyl compounds. It appears that the aliphatic content is higher than the aromatic content. The similarity of this spectrogram to Figure 1 is very apparent.

Whiting, Indiana Neutral Group (Figure 4)

(1) This spectrogram is very similar to the neutral fraction of the refinery extract (Figure 2).

(2) The major difference is the presence of a small carbonyl band and an OH band at 3300 cm^{-1}. The OH band is due to neutral OH groups.

Summary

The carbonyl band is of very low intensity and indicates small quantities of neutral carbonyl compounds. They may be esters and/or ketones and less likely aldehydes. Aliphatic and aromatic hydrocarbons are indicated.

Hammond, Indiana (Figure 5)

(1) This spectrogram is quite similar to the one obtained from Whiting raw water extract. Notable differences are the greater intensity of the OH band and the carbonyl band. More than one kind of carbonyl is indicated.

Summary

It is theorized that the increased carbonyl and OH absorption are due to organic acids. These acids may arise as the result of oxidation of refinery type wastes or may be due to other type wastes.

Chicago, Illinois Raw Water Extract and Neutral Extract (Figures 6 and 7)

(1) Examination of the Chicago extract spectrogram reveals general similarities to the other raw extract spectrograms. Because of the high oxygen content it is not known with certainty if the oxygen is integrally bound to the hydrocarbon portions or if it exists independently as oxygenated compounds in admixture with hydrocarbon material.

Summary

Because of the lack of material for chemical testing it is not possible to draw conclusions with any degree of certainty.

Indiana Harbor Ship Canal (Figure 8)

(1) With very minor difference this spectrogram would fit if superimposed on the one obtained from Whiting raw water.

Summary

The interpretations drawn for Whiting raw water appear valid here.

Oil Separator Effluent Fractions 1, 2, and 10 (Figures 9, 10 and 11)

The major aromatic compounds indicated in Figures 9 and 10 are o-xylene, m-xylene, and p-xylene. In addition, Figure 9 shows evidence of chloroform with bands at 1215 cm^{-1} and 750 cm^{-1}. Higher boiling hydrocarbons are the principal constituents of fraction 10 (Figure 11).

Biochemical Oxygen Demand and Oxygen Consumed

The biochemical oxygen demand and oxygen consumed determinations were made on the oil separator effluent extract to determine something of the oxidation characteristics of such materials by biological and chemical oxidation methods. Using a 1/10,000 dilution and dilution water properly seeded [10,11] and saturated with pure oxygen a B.O.D. of 182,800 p.p.m. was obtained. The dichromate reflux method of Moore [12] was used for the oxygen consumed test. An oxygen consumed value of 1,950,000 p.p.m. was obtained. Expressed more simply, approximately two parts of oxygen were required for the oxidation of one part of waste. The ratio of the biochemical oxygen demand to the oxygen consumed indicates that only a relatively small fraction of the carbon of these compounds can be oxidized biochemically in a five-day period by the normal flora and fauna of polluted water and sewage.

The fact that these materials are not readily oxidized by the normal microflora of sewage and polluted water may explain their apparent persistence in the lake water. Before definite conclusions can be reached additional studies on the possible biological oxidation of the extracts and the neutral fractions contained therein are needed. Studies on the persistence of these compounds in lake water within the normal temperature range, and in the presence of possible adaptive microflora, are also needed.

TASTE AND ODOR STUDY

All of the extracts obtained in the study were tested for odor thresholds. Taste tests were made on some of the samples. In addition to the raw extract, the amine, acidic, phenolic and neutral groups separated from the refinery separator effluent sample and the City of Whiting samples were tested for taste and odor characteristics.

Methods of Making Taste and Odor Tests

The various extracts were weighed carefully and solutions or suspensions of 20 to 25 p.p.m. were prepared using odor free water as the diluent. This solution was diluted to one p.p.m. The approximate range of the odor threshold was determined. A series of six to eight dilutions was prepared, using a 50 per cent interval of dilution. This series was presented to one, two or three observers with blank samples in the series so that the observers could not know which flasks contained odorous material. All tests were made at 30°C. ± 2°C. A typical odor series follows:

Observer	Concentration of Extract p.p.b.							
	3	6.2	Blank	12.5	25	Blank	50	100
A	-	-	-	-	+	-	+	+
B	-	+	-	+	+	-	+	+
C	-	+	-	+	+	-	+	+

Observer A was an experienced odor tester and followed all samples closely throughout the study. This observer has fair odor sensitivity and is reasonably constant from day to day. Observer B was relatively inexperienced and was much more sensitive to some odors than to others. Observer C was an experienced odor tester. High sensitivity is usually shown by this observer but he may be less sensitive on certain odors than Observer A. The odor results obtained by the three observers are presentedin Tables 7 and 7a. Taste tests were made in a similar manner. Taste tests are more difficult and it is believed less reliable than odor tests. Emphasis is placed on odor

testing in this study. It is believed that a threshold odor variation of several p.p.b. in these samples is insignificant. Different observers may vary this much and the same observer's sensitivity may vary from day to day by such quantities.

Discussion of Taste and Odor Results

It should be recognized that simple detection of odor or taste by laboratory tests does not establish the limiting concentration that may be expected to give taste and odor in the drinking water. The tests do serve to compare the taste and odor characteristics of various samples. A desirable drinking water should be free from any taste and odor, hence the least concentration of carbon adsorbate that can be detected by the sense of smell or taste may be used for comparison of the various extracts.

The extracts from the Indiana Harbor Ship Canal, the refinery waste effluent and the City of Whiting had very strong obnoxious odors best described as gasoline or refinery like. The extract from the Chicago raw water was detectable at a concentration of 13 p.p.b. It could not be said with certainty that the odor of this extract was similar to the others although some trace of refinery characteristics appeared to be present.

The amine, acidic, phenolic and neutral fraction of the refinery waste separator effluent and the City of Whiting extracts were also tested for taste and odor characteristics. The neutral fraction was shown to constitute approximately 85 per cent of the extract eluted from the oil separator effluent sample. This fraction and the raw extract had very similar odors. This same similarity was noted in the Whiting raw extract and neutral fraction extract. On the basis of the adsorbates tested there seems to be little doubt that the neutral compounds are the most important causes of taste and odor in

the waters of the South Lake Michigan area. Further study of filters at various stages of saturation should help to clarify such points as the relative contribution of various components in the water to taste and odor.

The odor of the materials recovered by the methods used in this study from wastes and the water was detectable in concentrations from 1 to 25 p.p.b. One pound of such an extract, with a threshold of 10 p.p.b., could give taste and odor to 12,000,000 gallons of water.

It is well known that minute concentrations of phenolic compounds, particularly chlorinated derivatives of phenol may produce serious taste and odor problems in water supplies. It will be noted from Table 5 that the phenolic compounds make up less than four per cent of the total extract. The presence of phenols may always be looked upon with suspicion in regard to taste and odor and every effort should be made to reduce the concentration of these compounds to a minimum. However, it is not believed that phenols are the principal cause of taste and odor in the South Lake Michigan area.

Effect of Chlorination on Taste and Odor

Studies were made on the effect of chlorination on the taste and odor characteristics of the refinery waste separator effluent extracts and the neutral and phenolic fractions of the same extract. A one p.p.m. solution of the extract was chlorinated so that a residual chlorine was present in the amount of 0.1 to 0.25 p.p.m. after two hours of contact. This solution was then diluted in the usual manner for making a taste and odor test.

As expected the phenolic fraction increased in taste and odor intensity with this amount of chlorination. Taste and odor were detectable in concentrations of two to six p.p.b. of the chlorinated materials. No attempt was made to superchlorinate or to run a breakpoint series on these materials.

Some idea of the effect of simple marginal chlorination on these materials was the aim of the test.

Chlorination of the raw extract from refinery separator effluent and the neutral fraction of the same extract showed little effect on the threshold odor. The chlorine appeared to reduce slightly or mask the disagreeable character of the odor and taste.

RECOMMENDATIONS

This study of the application of the carbon filter technique is necessarily incomplete. Parallel work at this Center with more active carbon in non-corroding filters* had demonstrated the possibility of substantially higher recoveries of organic materials in studies of this type. Experience obtained by this survey suggests additional work to extend the possibilities of the application of this procedure to other studies of this kind. Consequently, the following recommendations are made for consideration in any future investigations that may be undertaken:

(1) That the new carbon filters consisting of pyrex glass holders containing a much finer and more active carbon be used in place of the iron ones used in this study. Recovery of more materials would permit a detailed study of the chemical composition and quantities of various chemical groups present.

(*) It has been found during these studies that rust deposited on the active carbon impairs the absorption properties of the filter.

(2) That the effects of saturation of the carbon by adsorbed chemicals from such wastes as the refinery separator effluent be studied by passing from 500 to 2,500 gallons of effluent through several separate filters. Direct studies of the refinery separator effluent waste should be attempted. Such studies should show the effectiveness of the carbon filters in picking up representative samples of waste constituents.

(3) That samples be collected from several points of reference to establish more valid controls. The role of organic sulphur compounds in extracts from wastes and water needs further study.

(4) That the persistence and biochemical oxidizability of the neutral fraction from these extracts be studied in Lake Michigan waters.

SUMMARY AND CONCLUSIONS

(1) A study involving the application of the active carbon absorption and elution technique for concentration of organic compounds in water was made in the South Chicago area of Lake Michigan. This study demonstrated the importance of this technique for the concentration of organic materials and the useful application of organic group separation, elemental analysis and infrared spectroscopy to the adsorbates in studying a water pollution problem. The use of sulphur as a naturally occurring tracer element for selected wastes is indicated.

(2) The concentrations of organic constituents recovered in the untreated water in these locations were 495, 184, 89 and 22 parts per billion for the Indiana Harbor Ship Canal, Whiting, Hammond and Chicago South District Plant, respectively. The filter placed on the oil refinery separator effluent became saturated and, consequently, the organic concentrations obtained are considered too low.

(3) The organic material adsorbed by active carbon from the refinery waste separator effluent was shown to be a mixture of aliphatic and aromatic hydrocarbons with lesser amounts of phenols, acids, amines and sulphur compounds. The neutral hydrocarbon fraction represented roughly 84 per cent of this material.

(4) The organic material recovered by active carbon from the raw waters of the Indiana Harbor Ship Canal, Whiting and Hammond appear to be similar to the material recovered from the refinery separator effluent. The differences noted between the separator effluent material and the above mentioned raw water extracts may be attributed to oxidation of these wastes in contact with water, or admixture with other wastes or both of these causes.

(5) Conclusions regarding the character and origin of organic material recovered in the Chicago South District Filtration Plant raw water are not drawn at the present because of the small quantity of material recovered which prevented group separation and careful study.

(6) Taste and odor tests made on oil refinery separator effluent extract have demonstrated that the neutral fraction contributes disagreeable tastes and odors of high intensity. These odors are detectable by keen observers in concentrations of 5 to 10 parts per billion.

(7) On the basis of the quantities of materials recovered in the waters at Whiting and Hammond and the taste and odor studies made on the extracts, it must be concluded that quality of the drinking water source for these supplies is seriously affected by the organic constituents contained therein.

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TABLE NO. 1

Filter Operational Data

Location	Dates Activated Carbon Filter Was in Operation		Average Rate of Flow	Total Gallons Filtered
	From	To	G.P.M.	
Oil Separator Effluent	1-30-51	2-20-51	0.25	7,489
Indiana Harbor Canal	2-14-51	3-12-51	0.42	12,950
Whiting, Indiana Raw Water	1-29-51	2-26-51	0.516	20,160
Hammond, Indiana Raw Water	1-29-51	2-28-51	0.34	12,765
Chicago South District Filtration Plant	1-24-51	3-1-51	0.5	25,193

TABLE NO. 2

Quantities of Extract Recovered from Carbon Filters

Source of Sample	Total Anhydrous Organic Extract	
	grams	Parts per Billion
Oil Separator Effluent	369	13,000
Indiana Harbor Ship Canal	24.24	495
City of Whiting, Indiana	14.71	184
City of Hammond, Indiana	4.32	89
Chicago, Illinois South District Filtration Plant	2.14	22

TABLE NO. 3

Results of Elemental Analyses on Organic Extracts

Source of Sample	Carbon %	Hydrogen %	Nitrogen %	Sulphur %	Oxygen by Difference %	Ash %
Oil Separator Effluent	84.9	11.2	0.13	1.2	2.57	-
Indiana Harbor Ship Canal	67.4	10.7	0.33	2.2	19.37	-
City of Whiting, Indiana	76.4	9.2	0.26	1.5	12.64	-
City of Hammond, Indiana	74.4	10.3	0.24	2.2	12.86	-
Chicago, Illinois*	66.6	8.4	0.93	1.6	22.23	0.23
South District Filtration Plant	65.9	9.0	0.85	1.5	22.41	0.34
Cincinnati, Ohio (Finished Water Extract)	62.6	8.1	0.60	< 0.2	28.5	-

(*) Two layers were present in this extract and were tested separately

TABLE NO. 4

Properties of Fractional Distillates - Oil Separator Effluent Extract

Fraction No.	Refractive Index 25°C.	Boiling Point Range 18 mm. Hg Degrees C	Odor	Color	Fluorescence Under Black Light
1	1.4738	-	Mercaptan	Yellow	None
2	-	38°	Mercaptan	Clear Yellow	None
3	1.4738	40o	Hydrocarbon	Clear Yellow	None
4	1.4782	40.5°-49.5°	Hydrocarbon	Clear Yellow	None
5	1.4870	50°	Naphthalenic	Clear Light Brown	None
6	1.4938	50.5°-51°	Naphthalenic	Clear Brown	None
7	1.4953	51.5°-60°	Hydrocarbon	Clear Brown	Cream
8	1.4960	60.5°-66°	Hydrocarbon	Clear Brown	Brown
9	1.4970	66.5°-70°	Hydrocarbon	Clear Orange	Brown
10	1.4911	70.5°-76°	Acrid	Brown-ish Black	Green

TABLE NO. 5

Separation of Extracts from Oil Separator Effluent and Whiting Raw Water

Extract	Neutral Compounds	Phenolic Compounds	Acidic Compounds	Basic Compounds	Loss Unaccounted for
	Per cent	Per cent	Per cent	Per cent	Per cent
Oil Separator Effluent	84.5	3.73	0.15	0.44	11.18
Whiting Raw Water	45.09	0.47	0.63	0.80	52.87*

(*) The large unaccounted for loss obtained in this separation cannot be explained. Insufficient extract remained to repeat the separation.

TABLE NO. 6

Properties of Extracts and Extract Constituents

Sample	Refractive Index	Odor	Color	Fluorescence Under Black Light
Oil Waste Separator Effluent	1.5006	Refinery	Black	Brown
a. Neutral Group	1.5020	Refinery	Brown	Brownish-Black
b. Acid Group	-	Aromatic Caproic Acid	Brown	Red
c. Amine Group	-	Tobacco-like	Brown	Orange
d. Phenolic Group	-	Phenolic	Wine	Violet
Ship Canal	1.482	Refinery	Red	Light-Orange
Whiting, Indiana	1.496	Refinery	Reddish-Brown	Brown
a. Neutral Group	1.4491	Refinery	Red	Yellow
b. Acid Group	-	Caproic	Red	Deep Orange Brown
c. Amine Group	-	Pyridine-like		
d. Phenolic Group	-	Phenolic	Brown	Reddish
e. Insoluble Group	-	None	White	Purple
Hammond, Indiana	1.4905	Refinery	Red-Brown	Pink-Orange
Chicago, Illinois				
a. Layer 1	1.478	Aromatic	Yellow	-
b. Layer 2	1.552	Painty, Mild Hydro-carbon	Amber	-

TABLE NO. 7

Lowest Concentration of Organic Extract Detectable by Odor and Taste

Source of Extract	Parts per Billion Detected						Type of Odor at High Dilution
	Odor Observer			Taste Observer			
	A	B	C	A	B	C	
Refinery Waste Separator Effluent	13	25	3	25	13	-	Oil or gasoline
a. Chlorinated-R.W.S.E	6	25	13	25	-	-	Oily, less obnoxious than raw waste sample
b. Amine Fraction	8	8	3	-	-	-	Tobacco-like
c. Acid Fraction	1	-	1	10	-	-	Pleasant, fruity
d. Phenolic Fraction	31	250	-	500	-	62	Phenolic
e. Phenolic Fraction-Chlorinated	3	2	2	6	2	2	Chlorophenolic
f. Neutral Fraction	13	13	-	13	13	-	Oily, refinery
g. Neutral Fraction - Chlorinated	6	13	-	6	-	-	Oil, gasoline

TABLE NO. 7a

Lowest Concentration of Organic Extract Detectable

by Odor and Taste

Source of Extract	Parts per Billion Detected						Type of Odor at High Dilution
	Odor Observer			Taste Observer			
	A	B	C	A	B	C	
City of Whiting, Indiana Raw Water	10	20	-	10	5	-	Refinery
a. Amine Fraction	6	6	-	-	-	-	Tobacco-like
b. Acid Fraction	10	10	-	-	-	-	Aromatic
c. Phenolic Fraction	25	13	13	-	-	-	Phenolic
d. Neutral Fraction	5	10	5	-	-	-	Oily
Indiana Harbor Canal	1	3	-	5	5	-	Oily
City of Hammond, Indiana	20	40	-	40	40	-	Oily
City of Chicago, Illinois	13	13	13	100	13	-	Aromatic, not unpleasant

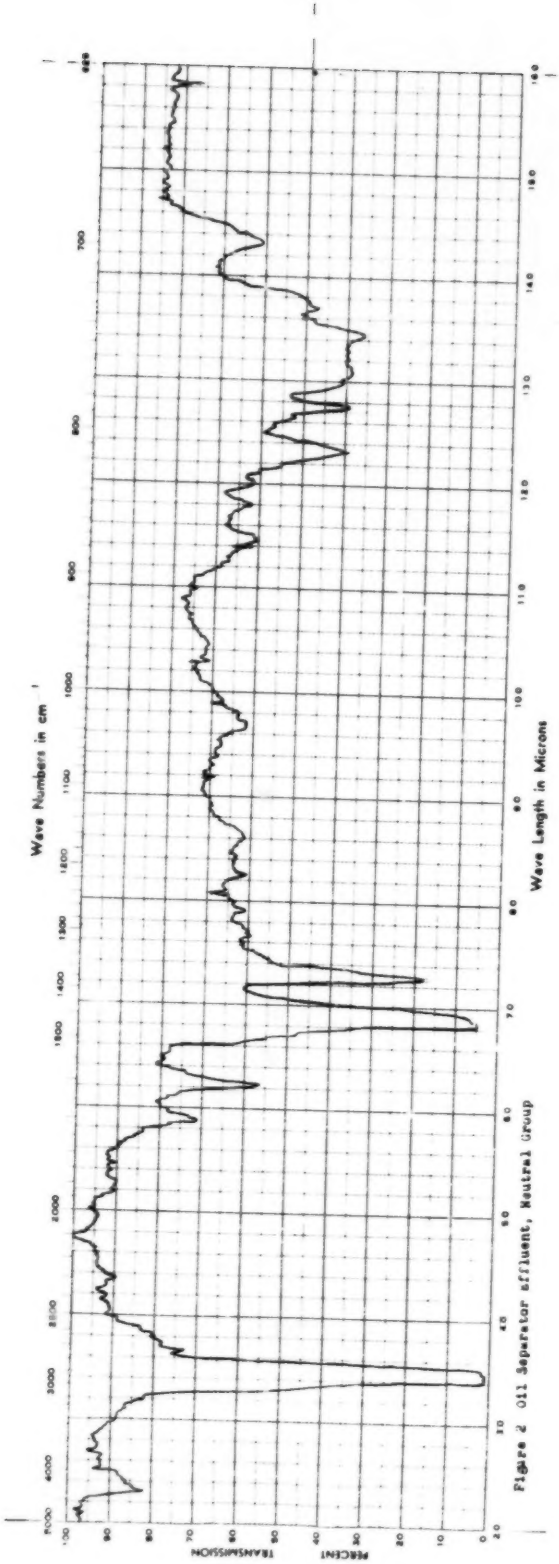

Figure 2 Oil Separator effluent, Neutral Group

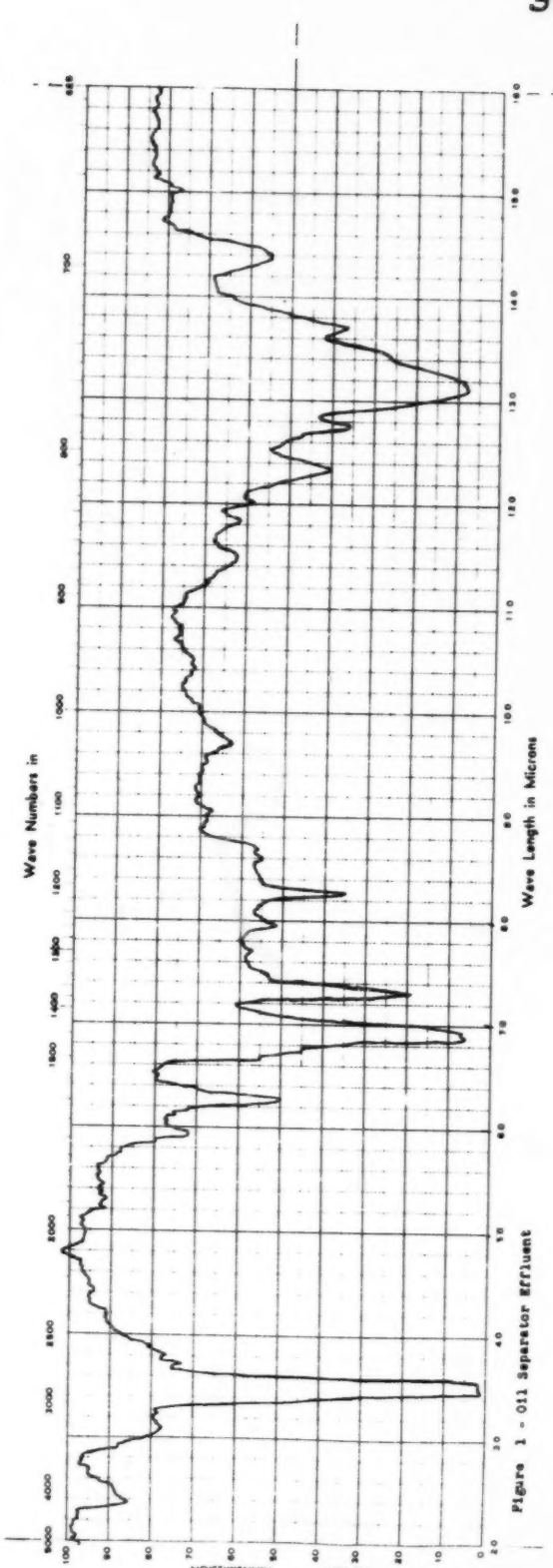

Figure 1 - Oil Separator Effluent

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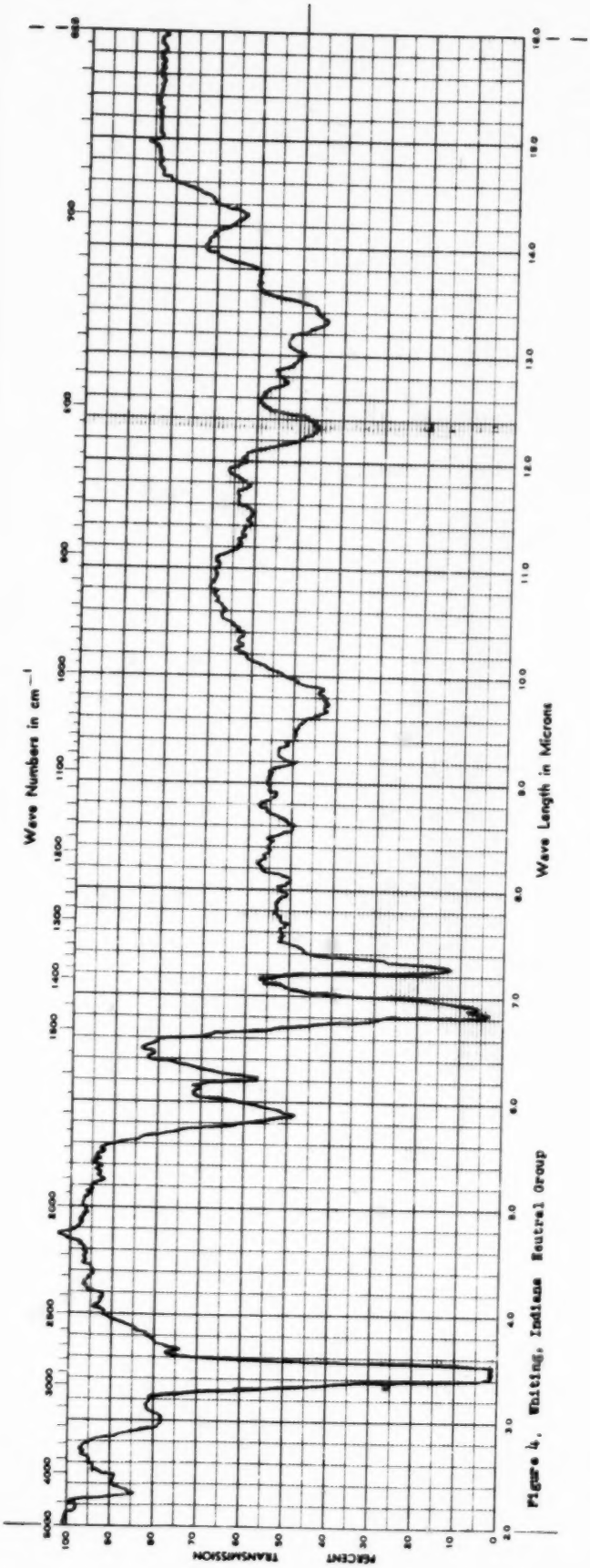

Figure 4. Whiting, Indiana Neutral Group

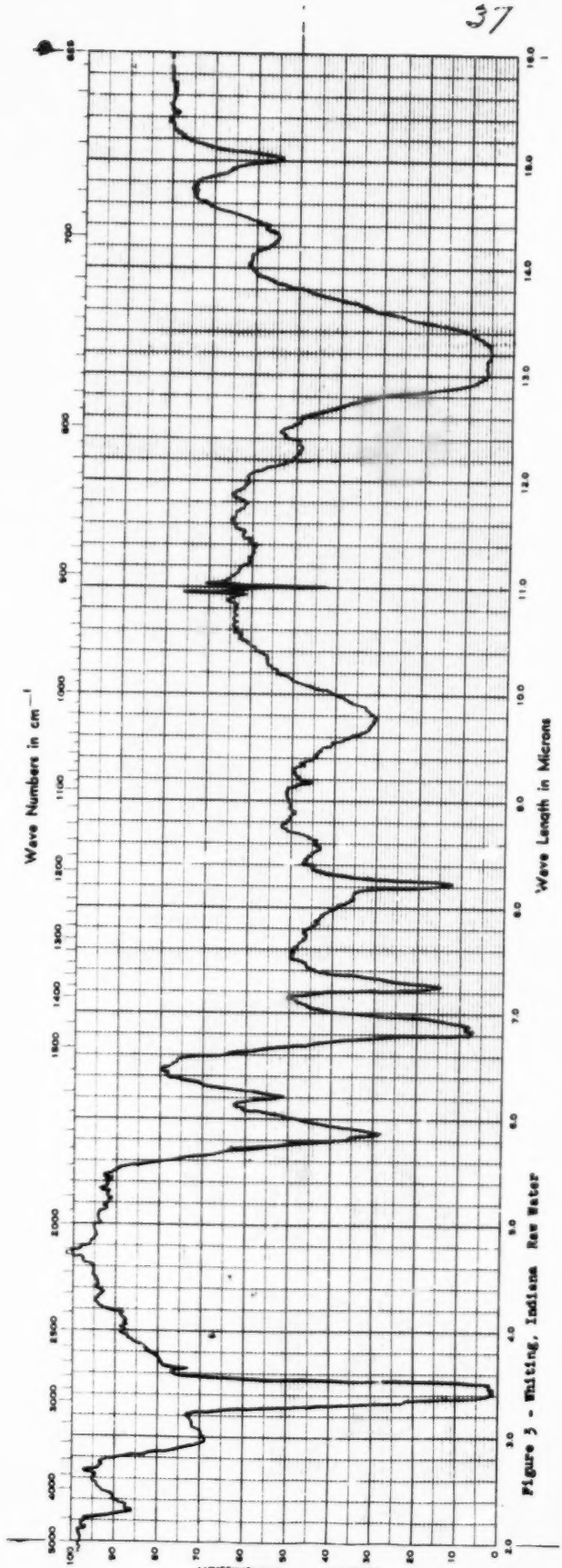

Figure 5 - Whiting, Indiana Raw Water

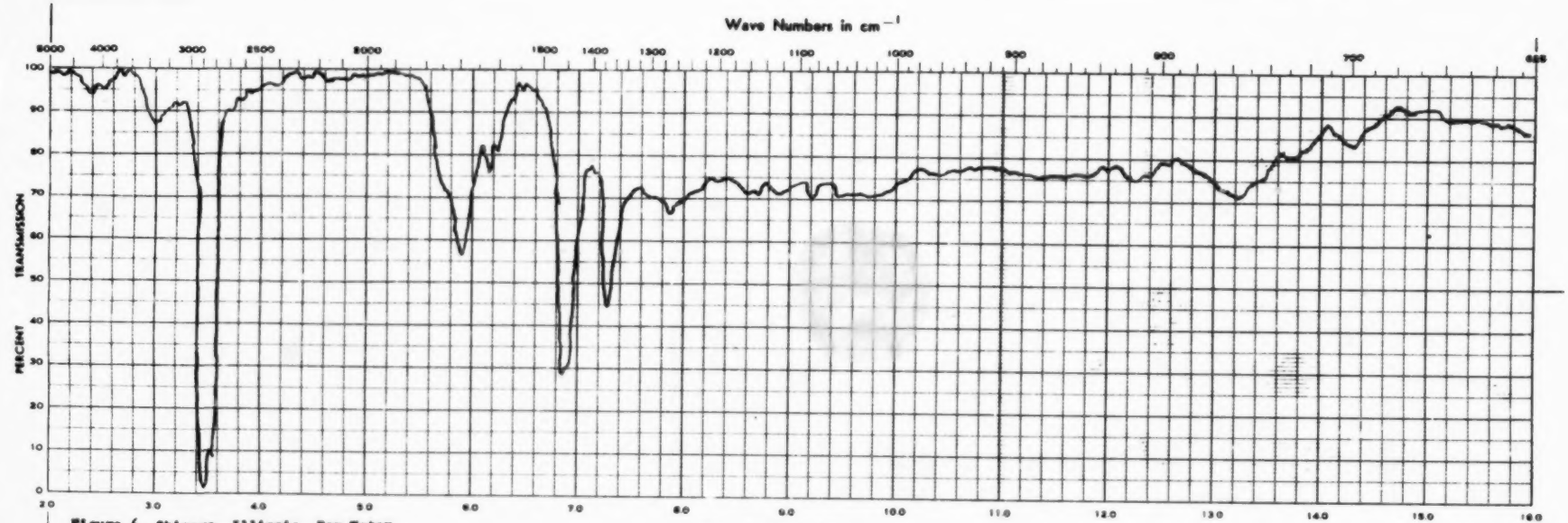

Figure 6, Chicago, Illinois Raw Water

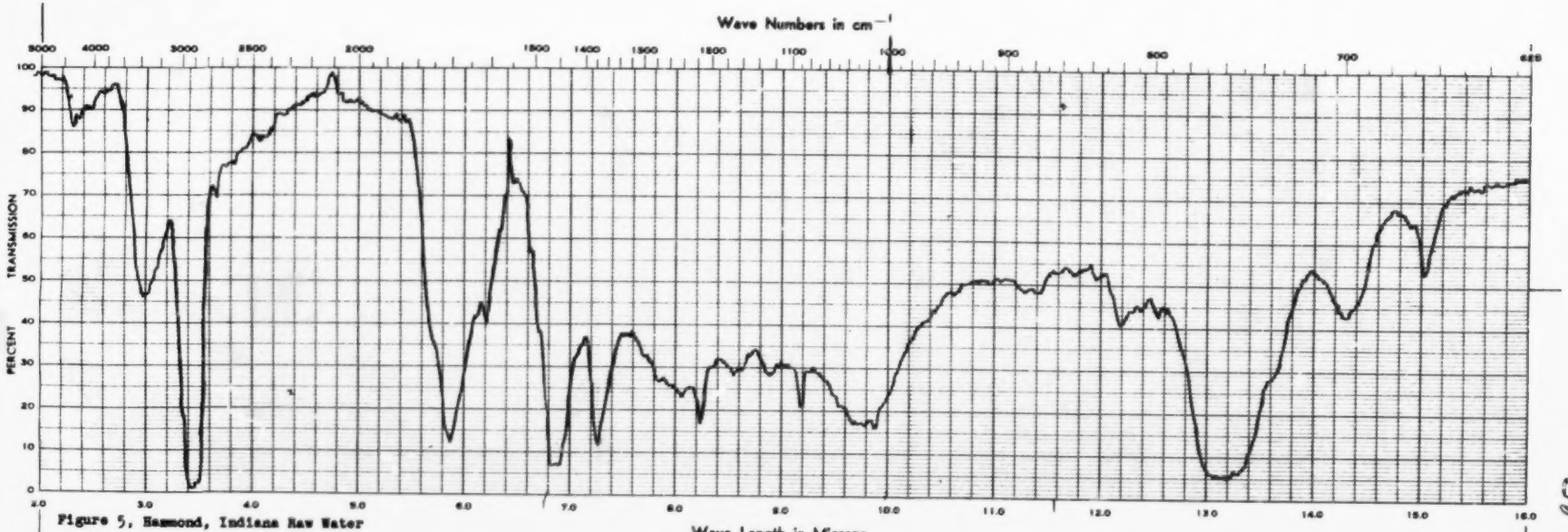

Figure 5, Hammond, Indiana Raw Water

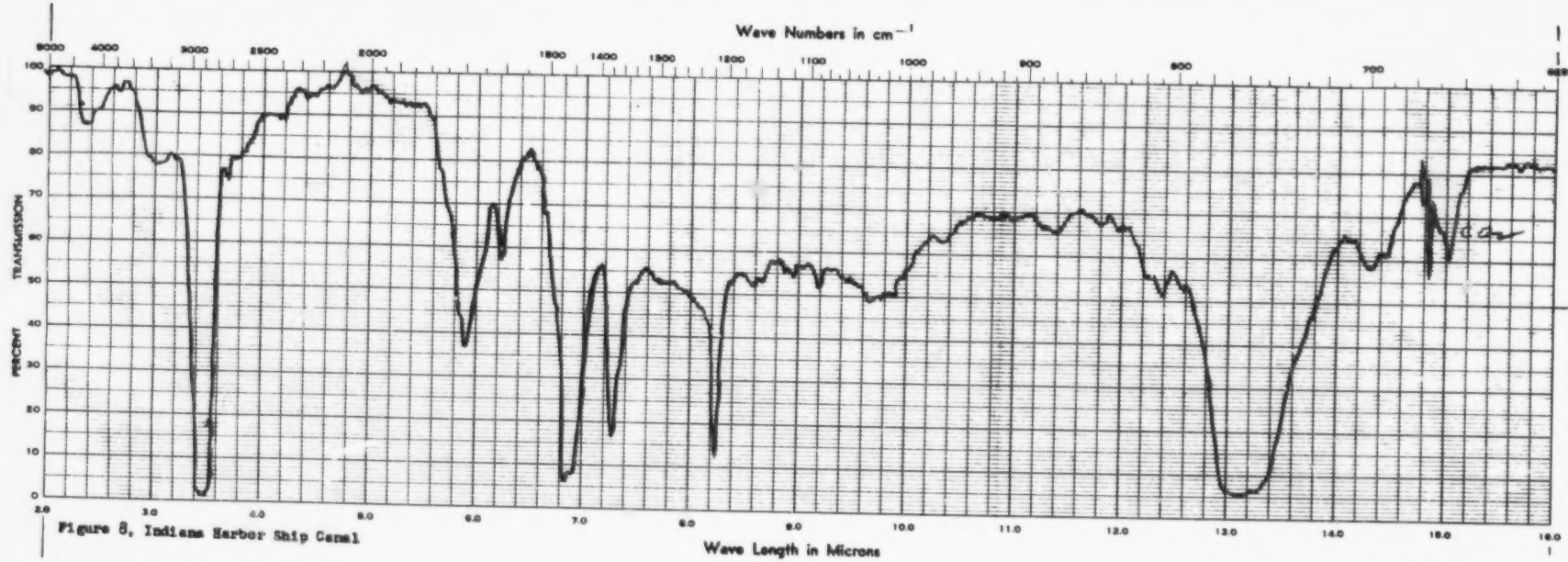

Figure 8, Indiana Harbor Ship Canal

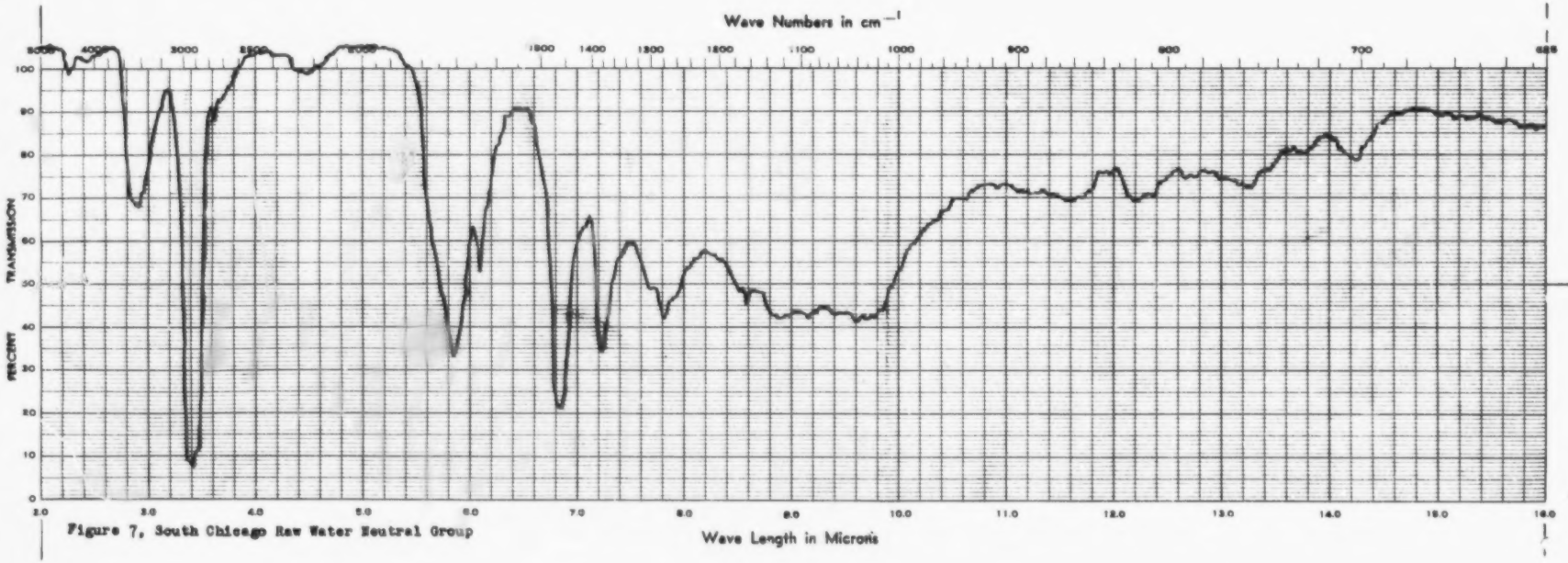

Figure 7, South Chicago Raw Water Neutral Group

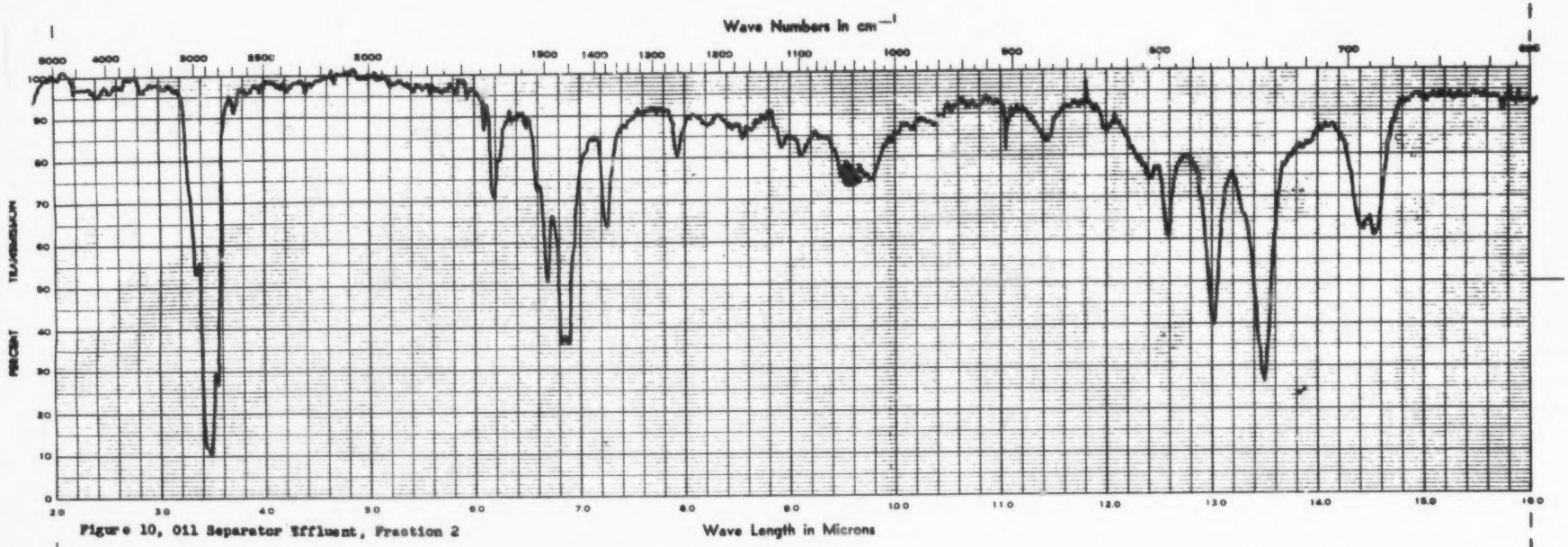

Figure 10, Oil Separator Effluent, Fraction 2

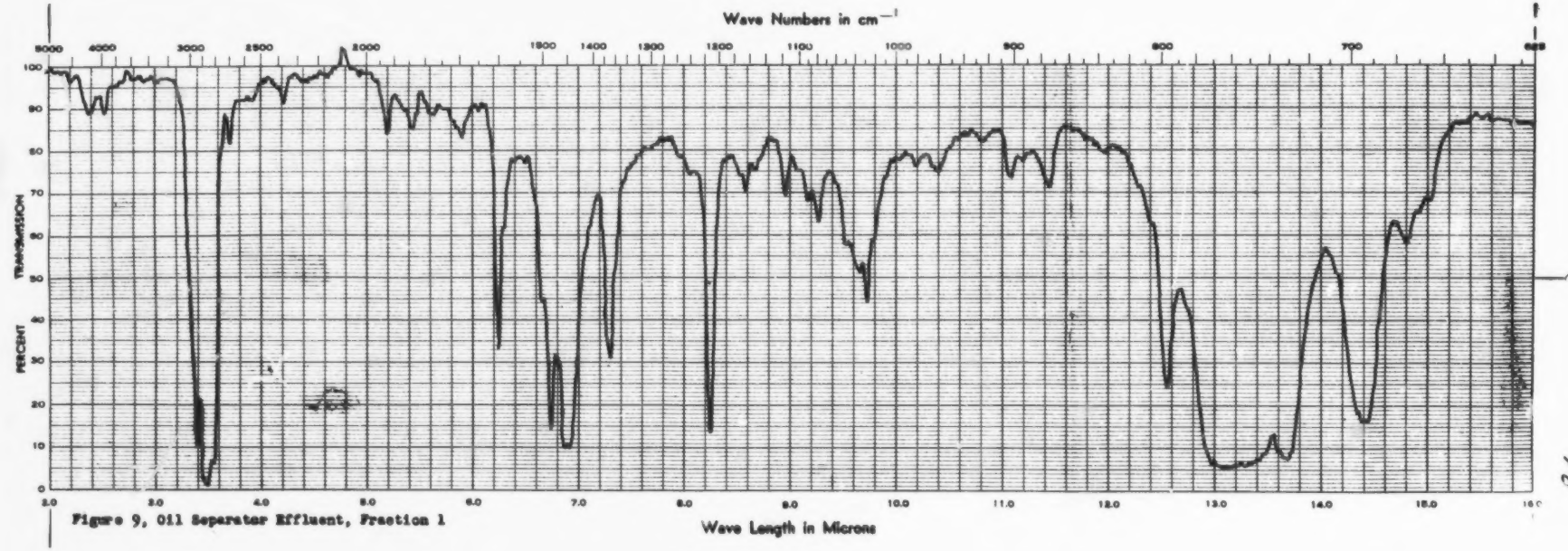

Figure 9, Oil Separator Effluent, Fraction 1

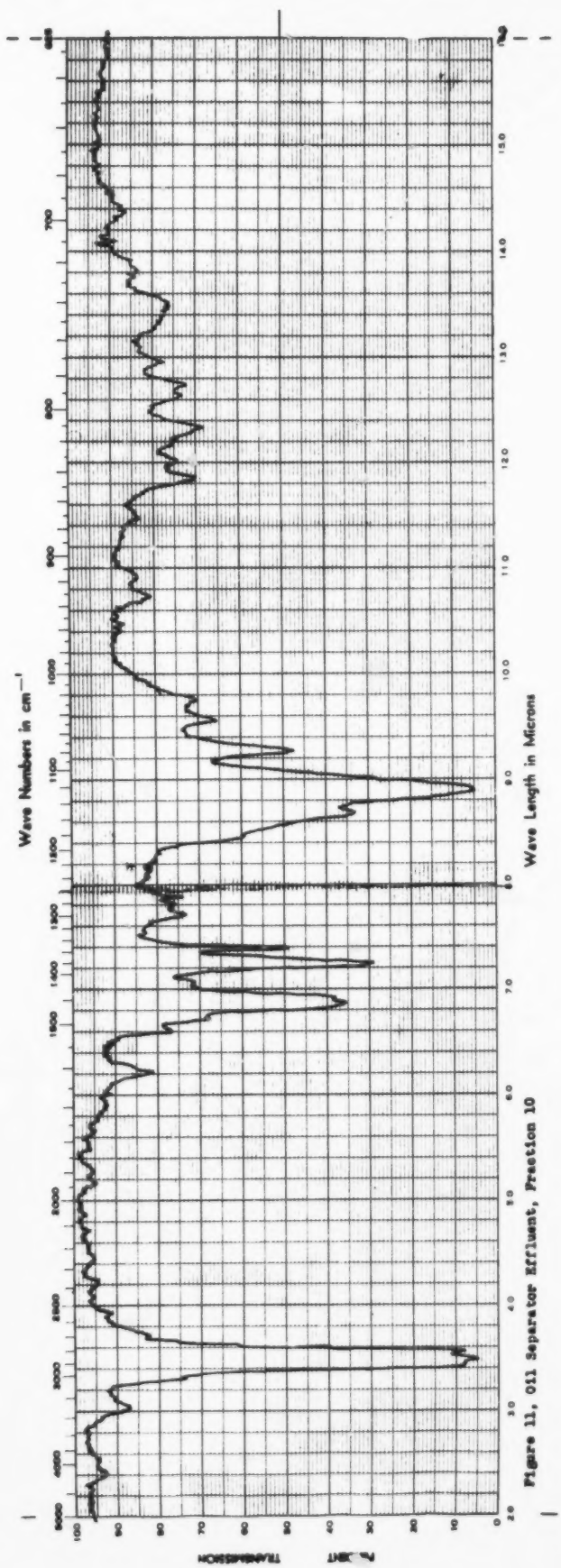

Figure 11, Oil Separator Effluent, Preston 10